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AUTHOR(S):

Doi, Tsunesuke

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PHYSICO-CHEMICAL PROPERTIES OF SULFUR

IV Critical Polymerization Temperatures and Polymerization
Equilibrium Constants of Sulfur

BY TSUNESUKE DOI

The critical transition temperature, at which the production of sulfur polymer starts abruptly, changes with the dilution of sulfur by inactive diluent. As to this process, some data obtained by measuring the viscosity-temperature behavior in a viscometer have already been reported by the author. By analysing these data by means of the equation of the degree of polymerization obtained by Tobolsky *et al.*, the author succeeded to get the polymerization equilibrium constants of sulfur, independent of the data of Tobolsky *et al.* The equilibrium constants thus obtained are somewhat lower than those of Tobolsky *et al.*

The plots of the logarithm of equilibrium constant *vs.* the reciprocal of absolute temperature become a straight line. From the slope and the intercept of this straight line, the numerical values of ΔH and ΔS for the polymerization of sulfur were obtained as 2790 cal. mole⁻¹ and 2.61 cal. deg⁻¹ mole⁻¹, respectively.

Introduction

In the previous papers^{1,2)}, the author used the numerical values obtained by Tobolsky³⁾ *et al.* for the equilibrium constants of sulfur polymerization. But the author wanted to obtain the constants independent of the data of Tobolsky *et al.*, because these values were important for the previous papers and it was necessary to examine the numerical values obtained by Tobolsky *et al.* from another point of view.

The author has already reported the data⁴⁾ related to the change of temperature at which the production of sulfur polymer starts abruptly. The critical temperature changes with the dilution of sulfur by inactive reagents. One of the purposes of this paper is to obtain, independent of the data of Tobolsky *et al.* the equilibrium constants of sulfur polymerization, by analysing the data mentioned above, by means of the equation of polymerization degree obtained by Tobolsky *et al.* Another purpose is to obtain the values of ΔS and ΔH for sulfur polymerizations from the straight line obtained by the plots of the logarithm of equilibrium constants against the reciprocal of absolute temperatures. The results are compared with the data of other authors.

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- 1) T. Doi, *This Journal*, **33**, 41 (1963)
- 2) T. Doi, *ibid.*, **35**, 1 (1965)
- 3) A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.*, **81**, 780 (1959)
- 4) T. Doi, *This Journal*, **35**, 11 (1965)

Critical Polymerization Temperatures and Calculation of Polymerization Equilibrium Constants of Sulfur

In the paper of Gee⁵⁾, 159°C was selected as the critical transition temperature of polymerization, at which the polymer production of pure sulfur starts abruptly. This would be an adequate selection, because it is in accordance with the temperature of the intersecting point of the tangents of both sides of the sharp curvature of the viscosity-temperature curve of pure sulfur. The critical transition temperature of polymerization changes with the addition of the diluent to sulfur, as already mentioned.

The data related to the critical transition temperatures of polymerization were analysed by means of the equation derived by Tobolsky *et al.* According to the theory of polymerization equilibrium by Tobolsky *et al.*³⁾, the degree of polymerization is written as

$$P = \frac{1}{1 - KM} \quad (1)$$

where K is polymerization equilibrium constant (cf. reference 4), in which $K \equiv K'_3$) and M is monomer concentration. Eq. (1) should be effective, having nothing to do with as to whether a diluent co-exists with polymer. Using the suffix 0 to denote the system without diluent, eq. (1) becomes

$$P_0 = \frac{1}{1 - K_0 M_0} \quad (2)$$

At the corresponding points of both eqs. (1) and (2), we obtain

$$P = P_0 \quad (3)$$

Especially in the immediate upper neighbourhood of the critical transition temperature of polymerization, the degrees of polymerization of sulfur in the systems both with and without diluent should be very high, and both are considered to be the same. Therefore, we obtain

$$KM = K_0 M_0.$$

According to the thermodynamics, we obtain

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

$$\ln K_0 = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT_0} \quad (5)$$

where ΔS and ΔS_0 are the entropies of polymerization of the systems both with and without diluent, respectively, and ΔH and ΔH_0 are the corresponding enthalpies of polymerization, respectively. In general, strictly speaking, ΔS and ΔH are not the same as ΔS_0 and ΔH_0 , respectively. But if we substitute both K and K_0 from eqs. (4) and (5), respectively, into eq. (3), regarding as $\Delta S = \Delta S_0$ and $\Delta H = \Delta H_0$ approximately, we obtain

5) G. Gee, *Trans. Faraday Soc.*, **48** 515 (1952)

$$\frac{1}{T} = \frac{1}{T_0} - \frac{R}{\Delta H_0} \ln \left(\frac{M_0}{M} \right). \quad (6)$$

Eq. (6) is identical with one of Gee⁶⁾, with the exception of the unit of the concentration. In the immediate upper neighbourhood of the critical transition temperature of polymerization, we may assume $P=\infty$ and we may also assume that the monomer concentration is the same as the initial one. Therefore, from eq. (1), we obtain

$$K = \frac{1}{M}. \quad (7)$$

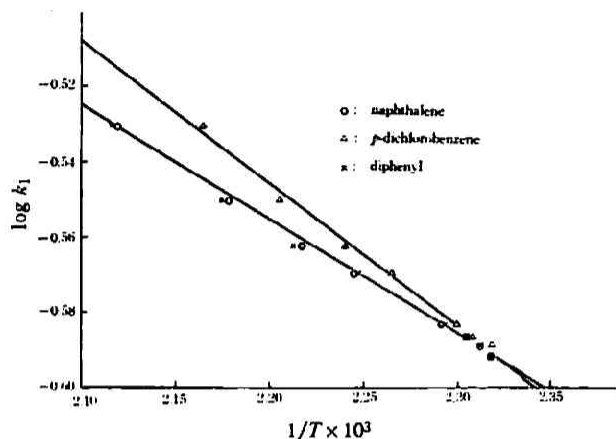
The equilibrium constants could be calculated by substituting the numerical values of the paper (cf. Table 2 of reference 4) into eq. (7). The results are shown in Table 1. With each system of different dilution, the values of the equilibrium constant and the corresponding absolute temperature are obtained from Table 1. The log-log plots of the equilibrium constants against the reciprocal of absolute temperatures were found to be linear. We can obtain ΔS and ΔH from the intercept and the slope of the straight

Table 1 Calculations of equilibrium constants

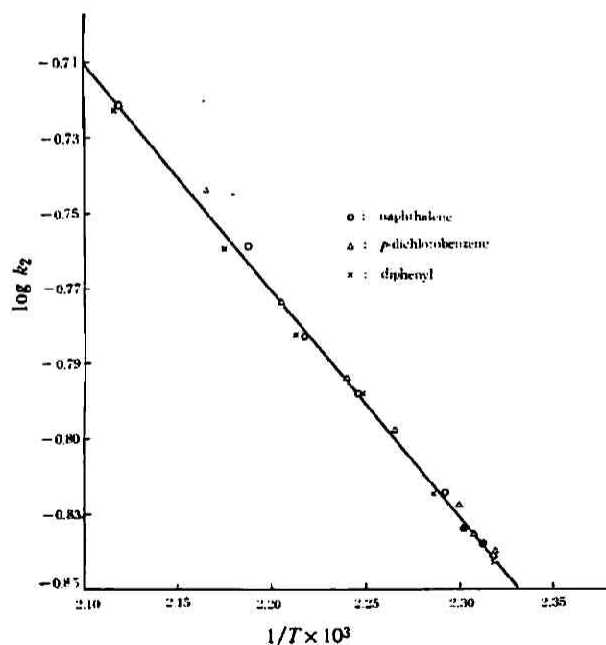
Naphthalene	Conc. of sulfur	M_k (mole/kg)	3.90	3.88	3.86	3.83	3.71	3.65	3.55	3.39
		$1/M_k \times 10$	2.564	2.577	2.591	2.611	2.695	2.740	2.817	2.950
		$\log 1/M_k$	-0.5911	-0.5889	-0.5865	-0.5833	-0.5694	-0.5622	-0.5502	-0.5302
		M_1 (mole/l)	6.95	6.88	6.81	6.67	6.28	6.06	5.73	5.26
		$1/M_1 \times 10$	1.439	1.454	1.468	1.499	1.592	1.650	1.745	1.901
		$\log 1/M_1$	-0.8420	-0.8374	-0.8332	-0.8241	-0.7980	-0.7822	-0.7583	-0.7210
<i>p</i> -dichlorobenzene	Conc. of sulfur	M_k (mole/kg)	3.90	3.88	3.86	3.83	3.71	3.65	3.55	3.39
		$1/M_k \times 10$	2.564	2.577	2.591	2.611	2.695	2.740	2.817	2.950
		$\log 1/M_k$	-0.5911	-0.5889	-0.5865	-0.5832	-0.5694	-0.5622	-0.5502	-0.5302
		M_1 (mole/l)	6.95	6.89	6.84	6.72	6.42	6.22	5.94	5.54
		$1/M_1 \times 10$	1.439	1.451	1.462	1.488	1.558	1.608	1.684	1.805
		$\log 1/M_1$	-0.8420	-0.8392	-0.8350	-0.8273	-0.8075	-0.7938	-0.7736	-0.7435
Diphenyl	Conc. of sulfur	M_k (mole/kg)	3.90	3.88	3.86	3.83	3.71	3.65	3.55	3.39
		$1/M_k \times 10$	2.564	2.577	2.591	2.611	2.695	2.740	2.817	2.950
		$\log 1/M_k$	-0.5911	-0.5889	-0.5865	-0.5832	-0.5694	-0.5622	-0.5502	-0.5302
		M_1 (mole/l)	6.95	6.88	6.81	6.67	6.28	6.06	5.74	5.28
		$1/M_1 \times 10$	1.439	1.454	1.468	1.499	1.592	1.650	1.742	1.894
		$\log 1/M_1$	-0.8420	-0.8374	-0.8332	-0.8241	-0.7980	-0.7822	-0.7590	-0.7226
	Critical trans. temp.	T (°K)	431.5	432.5	434.0	436.5	445.5	451.0	459.5	472.0
		$1/T \times 10^3$	2.318	2.312	2.304	2.291	2.245	2.217	2.177	1.119
<i>p</i> -dichlorobenzene	Conc. of sulfur	M_k (mole/kg)	3.90	3.88	3.86	3.83	3.71	3.65	3.55	3.39
		$1/M_k \times 10$	2.564	2.577	2.591	2.611	2.695	2.740	2.817	2.950
		$\log 1/M_k$	-0.5911	-0.5889	-0.5865	-0.5832	-0.5694	-0.5622	-0.5502	-0.5302
		M_1 (mole/l)	6.95	6.89	6.84	6.72	6.42	6.22	5.94	5.54
		$1/M_1 \times 10$	1.439	1.451	1.462	1.488	1.558	1.608	1.684	1.805
		$\log 1/M_1$	-0.8420	-0.8392	-0.8350	-0.8273	-0.8075	-0.7938	-0.7736	-0.7435
Diphenyl	Conc. of sulfur	M_k (mole/kg)	3.90	3.88	3.86	3.83	3.71	3.65	3.55	3.39
		$1/M_k \times 10$	2.564	2.577	2.591	2.611	2.695	2.740	2.817	2.950
		$\log 1/M_k$	-0.5911	-0.5889	-0.5865	-0.5832	-0.5694	-0.5622	-0.5502	-0.5302
		M_1 (mole/l)	6.95	6.88	6.81	6.67	6.28	6.06	5.74	5.28
		$1/M_1 \times 10$	1.439	1.454	1.468	1.499	1.592	1.650	1.742	1.894
		$\log 1/M_1$	-0.8420	-0.8374	-0.8332	-0.8241	-0.7980	-0.7822	-0.7590	-0.7226
	Critical trans. temp.	T (°K)	431.5	432.5	434.0	438.0	445.0	452.4	460.0	472.5
		$1/T \times 10^3$	2.312	2.312	2.304	2.283	2.247	2.212	2.174	2.116

6) F. Fairbrother, G. Gee and G. T. Merrall, *J. Poly. Sci.*, **16** 459 (1955)

line, respectively. The concentration unit of Fig. 1 is shown in mole kg^{-1} . Both naphthalene and diphenyl are plotted on the same straight line whose slope is somewhat less steep compared with *p*-dichlorobenzene. On the other hand, the concentration unit of Fig. 2 is shown in mole l^{-1} . In this case, the three diluents mentioned above are plotted on the same straight line. The numerical values of ΔS and ΔH obtained

Fig. 1 $\log K_1$ vs. $1/T$

K_1 refers to a standard state of 1mole/kg.

Fig. 2 $\log K_2$ vs. $1/T$

K_2 refers to a standard state of 1mole/l.

Table 2 ΔH and ΔS of sulfur polymerization

	Standard state	Experimental condition	ΔH ($\frac{\text{cal.}}{\text{mole}}$)	ΔS ($\frac{\text{cal.}}{\text{deg. mole}}$)
Gee <i>et al.</i>	—	Specific heat of pure sulfur	3180	7.4
Tobolsky <i>et al.</i>	1 mole/kg	Polymerization of pure sulfur	3170	4.63
Doi	1 mole/l	Polymerization of diluted sulfur	2790	2.61

from this straight line are shown in Table 2. The data of Gee *et al.* and those of Tobolsky *et al.* are shown in the Table for comparison.

Gee *et al.*⁵⁾ have tried to examine the effects of diluents on the sulfur polymerization. By measuring the volume-temperature behavior in a dilatometer, they obtained the result that the addition of 10% of naphthalene raised the critical transition temperature by approximately 10 degrees, as required by eq. (6). In their equation they assumed $\Delta H = 3200 \text{ cal. mole}^{-1}$ and that M and M_0 are shown in weight fractions of monomer in the liquid. This does not correspond to the author's results. According to the author's results mentioned above, the addition of 10 weight % of naphthalene raised the critical transition temperature by 28 degrees by the measurements of the viscosity-temperature behavior in a viscometer.

To the author's regret Gee *et al.* did not write the details of their experiments. But they wrote that naphthalene was not an ideal diluent, because it was attacked slowly by liquid sulfur as found by the smell of H_2S . But the author found that naphthalene added into liquid sulfur was stable against heat and that the viscosity curve was reproducible, (cf. the author's former article in this journal). Furthermore, according to the author's calculation by eq. (6), the addition of 10 weight % of naphthalene raised the critical temperature by 26 degrees, if ΔH is $2790 \text{ cal. mole}^{-1}$ and if the units of M and M_0 are shown in the mole fraction of monomer in the liquid. (The values of $\frac{M}{M_0}$ shown in both mole fraction and mole l^{-1} are almost the same in the liquid sulfur diluted with naphthalene.) Both experimental and theoretical values are shown in Table 3 and plotted in Fig. 3. The comparison shows excellent agreement.

Table 3 Calculation of critical transition temperatures of polymerization of diluted sulfur

Quantity of Naphthalene added (% to sulfur)		0.5	1.0	2.0	5.0	7.0	10.0	15.0
Sulfur conc. (mole fraction)		0.990	0.980	0.965	0.910	0.875	0.834	0.770
Cr. trans. temp. ($T_g^\circ \text{K}$)		433	435	437	445	451	458	470
$T_g - T_{g0}^*$	Calculated	1	3	5	13	19	26	38
	Observed**	1.0	2.5	5.0	14.0	19.5	28.0	40.5

*; $T_{g0} = 432^\circ \text{K}$

**; See Table 2 of reference 4)

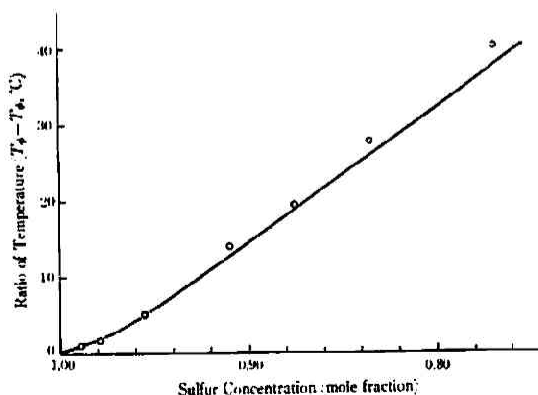


Fig. 3 $T_g - T_{g0}$ vs. M

—; calculated by eq. (1)

○; observed

Consideration

The author has succeeded to derive the equation which enables him to analyse his data⁴⁾, which is related to the changes of critical transition temperature depending upon the dilution of sulfur by inactive diluents, and which are obtained by measuring the viscosity-temperature behavior in a viscometer. The equation thus derived is identical with that of Gee *et al.* with the exception of the unit of the concentration. But the derivation is independent of their method. The comparison between the experiment and theoretical values shows excellent agreement, but the numerical values of the author and those of Gee *et al.* are considerably discrepant. The method of measurements and the unit of sulfur concentration for the calculation used by Gee *et al.* are not comprehensible to the author.

The author, furthermore, obtained the equilibrium constants of sulfur polymerization by applying eq. (1) of Tobolsky *et al.* for the degree of polymerization to the same data. In this case it is reasonable to use not mole kg⁻¹ but mole l⁻¹, because the specific gravities of diluents are considerably different from that of sulfur. Tobolsky *et al.*³⁾ adopted mole kg⁻¹ in their report. The author¹⁾²⁾ also adopted the same unit in his papers. In the case of pure sulfur only, it could be left out of consideration whether mole kg⁻¹ or mole l⁻¹ should be adopted, because, as to the specific gravities, there is hardly any difference between sulfur monomer and polymer, and because the specific gravities are slightly dependent on the temperatures. Therefore, those authors perhaps, as the author, adopted mole kg⁻¹, because it was helpful for the calculation.

The numerical values of equilibrium constant obtained by Tobolsky *et al.* must be divided by 1.75, the mean specific gravity in the temperature range 160 to 200°C, in order to be compared with the values of the author. The comparison is shown in Fig. 4. The author's data are plotted somewhat smaller than

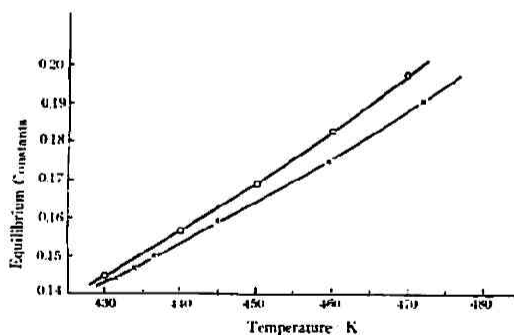


Fig. 4 Temperature dependences of equilibrium constant

○: Tobolsky *et al.*
×: Doi

that of Tobolsky *et al.* But the differences are negligible. The values from 0.4 to 0.7, the exponent obtained previously, become 0.5 to 0.9, if the exponents of the intrinsic viscosity-degree of polymerization relationships of sulfur published²⁾ previously are re-calculated with the smaller numerical values of equilibrium constants by approximately 5% with reference to Fig. 4. This does not affect the previous conclusion. The newly obtained values are on the contrary more useful in the light of the data of many other types of polymers.

As for the numerical values of ΔH of polymerization shown by the slope of straight line obtained by plotting $\log K$ vs. T^{-1} , the same value is obtained even if the unit of concentration and that of the

equilibrium constant are changed, if the specific gravity of the system remains the same. On the other hand, as for the numerical value of ΔS of polymerization shown by the intercept of the straight line, the numerical values would be different, if the unit of concentration and the unit of equilibrium constant are changed. If the unit of equilibrium constant is the reciprocal of concentration, the relationship between ΔS_1 shown in mole l^{-1} and ΔS_2 shown in mole kg^{-1} is given by

$$\ln \rho = \frac{1}{R}(\Delta S_2 - \Delta S_1) \quad (8)$$

where ρ is the specific gravity of the system, and R is the gas constant.

Therefore, ΔH obtained by Tobolsky *et al.* can be compared with that of the author because the specific gravities of the system change slightly, but ΔS obtained by Tobolsky *et al.* must be corrected by eq. (8) in order to be compared with that of the author. Correcting 4.63 cal. deg^{-1} of Tobolsky *et al.* by eq. (8), we obtain 3.91 cal. deg^{-1} . It can be concluded, that as to the numerical values of ΔH , there is no significant difference between Tobolsky *et al.* and the author. but that, in the case of ΔS , there is some difference. The numerical value of ΔS obtained by Gee *et al.* is a considerably higher estimate than that of Tobolsky *et al.* and of the author.

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